REPORT DOCUMENTATION PAGE

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MEMORANDUM FOR PRS (In-House/Contractor Publication)

FROM: PROI (STINFO) 19 Apr 2001

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-VG-2001-096**
Shawn H. Phillips; Timothy S. Haddad; Rusty L. Blanski, "New Multi-Functional Materials Using Versatile Hybrid (Inorganic/Organic) POSS Nanotechnology"

International Symposium – SAMPE **(Statement A)**
(Long Beach, CA, 08 May 2001) (Deadline: 08 May 01)

1. This request has been reviewed by the Foreign Disclosure Office for: a.) appropriateness of distribution statement, b.) military/national critical technology, c.) export controls or distribution restrictions, d.) appropriateness for release to a foreign nation, and e.) technical sensitivity and/or economic sensitivity.
Comments:____________________________________

Signature ____________________ Date __________

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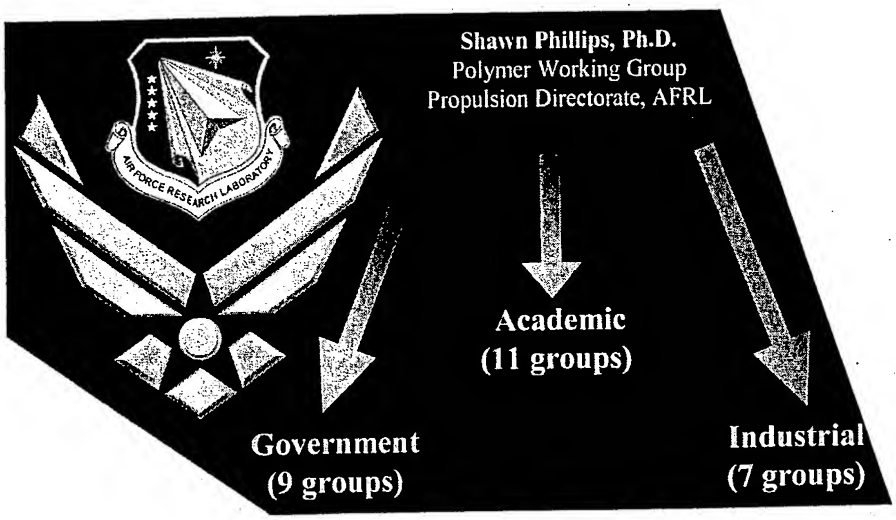
Comments:____________________________________

APPROVED/APPROVED AS AMENDED/DISAPPROVED

____
PHILIP A. KESSEL Date
Technical Advisor
Space and Missile Propulsion Division

New Multi-Functional Materials Using Versatile Hybrid (Inorganic/Organic) POSS ~~Nano~~technology
Angstro™



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Edwards
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- Mr. Hieu Nguyen

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- Dr. Joe Schwab - HP
- Prof. Pat Mather - UConn
- Dr. Jeff Gilman* - NIST
- Prof. Ben Hsiao - SUNY SB
- Prof. Bryan Coughlin* - UMass
- Prof. Gar Hoflund - UF
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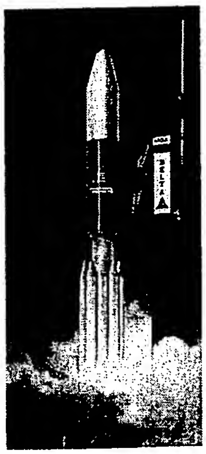
- Dr. Seng Tan - WMR
- Prof. Mark Gordon* - Iowa St. U
- Dr. Howard Katzman - Aerospace
- Mr. Don Geidt/Mike Blair - CSD/Thiokol

Funding: AFOSR (Dr. Charles Lee), AFRL, Hybrid Plastics

Basic R&D Applications R&D

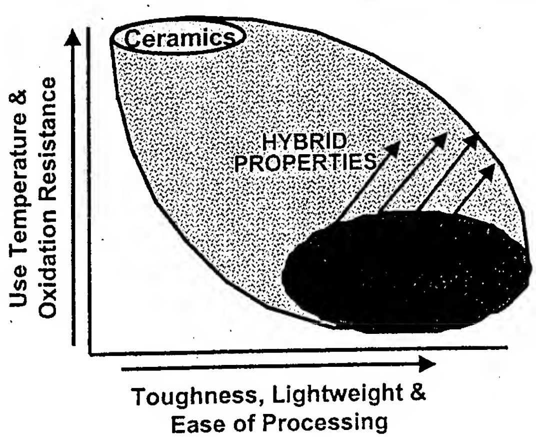
"Hot" Topics in Propulsion/Air Force Materials

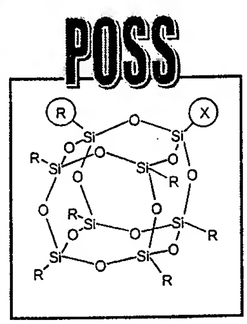


POSS Nanostructured Polymers

- High Temperature Insulation for Solid Rocket Motors
- Capacitors
- High Temperature/Lightweight Jet Canopies
- Space-survivable Materials and Coatings
- Low/High Temp. Hybrid Lubricants
- Plastic Tubing and Ducting for Liquid Rocket Engines
- High Temperature/High Translation Strength Composites
- Improved Radome Materials

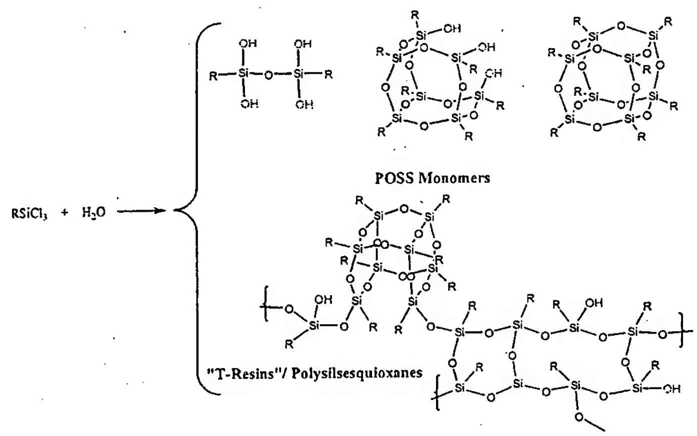
Multiple Applications/ Multi-Function





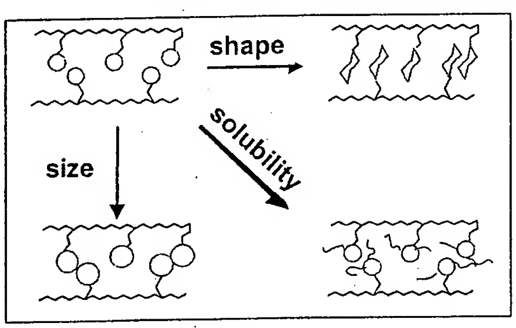
- Improve High Performance Polymers
- Transform Commodity Polymers into High performance Polymers
- Develop Multi-Functional Materials

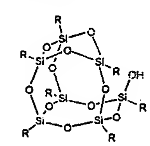
POSS Feedstocks



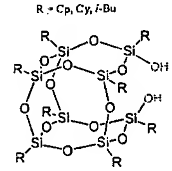
- R = Cyclohexyl, t = 3-36 (48 months)
- R = Cyclopentyl, t = 11 days!
- No other incompletely condensed silsesquioxanes

Existing POSS-Polymers: Structure/Property Relationships

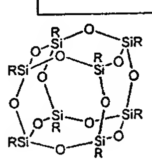




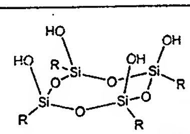
R = Cp, Cy, *i*-Bu



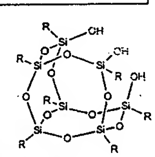
R = Cy, Cp, i-Bu, Et



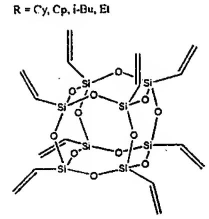
R_8T_8

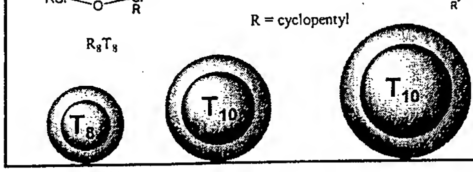


R = cyclopentyl



R = *i*-Butyl, Et





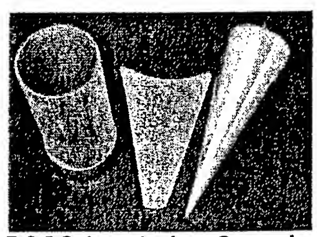
Property Enhancements via POSS

Observed in POSS-Copolymers and Blends

increased T_g	increased T_{dec}	enhanced blend miscibility
reduced flammability	extended temperature range	oxidation resistance
reduced heat evolution	increased oxygen permeability	altered mechanicals
lower density	lower thermal conductivity	reduced viscosity
disposal as silica	thermoplastic or curable	Beat competitors' patents !

6.2 (IHPRPT): Solid Rocket Motor Insulation

Case Insulation



POSS-Insulation Sample

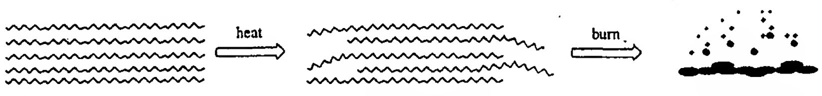
Goal: 50% Lower Erosion of Insulation (44 % weight reduction, 7.4% booster payload increase) – Phase III IHPRPT
Objective: Development of Ceramic Forming Polymer

POSS-Polymer Insulation - Advantages:

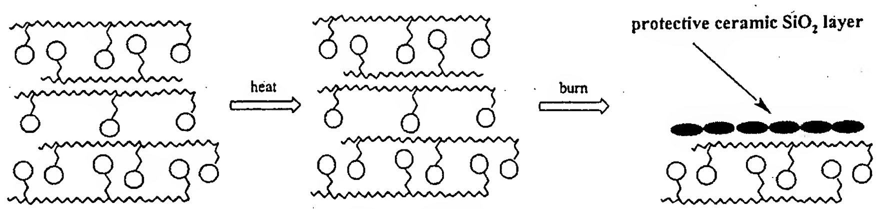
- High loadings of POSS can be incorporated without embrittlement
- Si to O ratio is 1:1.5, proven to oxidize up to 1:2 (SiO_2)
- Tailorability of POSS monomers improve physical/mechanical properties
- Capabilities for Large and Small scale testing (Hybrid Plastics)

POSS for Flame Retardant Materials

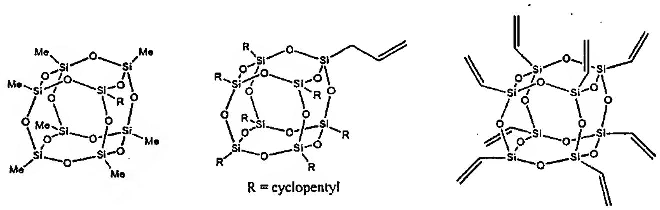
Traditional Polymer



POSS Polymer



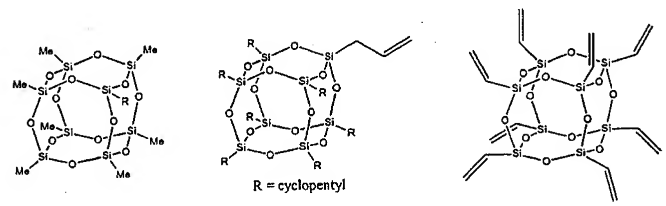
Comparisons of POSS in EPDM



At 25 wt% loadings relative to a proprietary base-line material

Hardness:	12%↑	no change	no change
Tensile:	17%↓	17%↓	---
Elongation:	no change	no change	no change
Viscosity:	42%↓	39%↓	36%↓
Density:	9%↑	3% ↓	3% ↓

Comparisons of POSS in EPDM



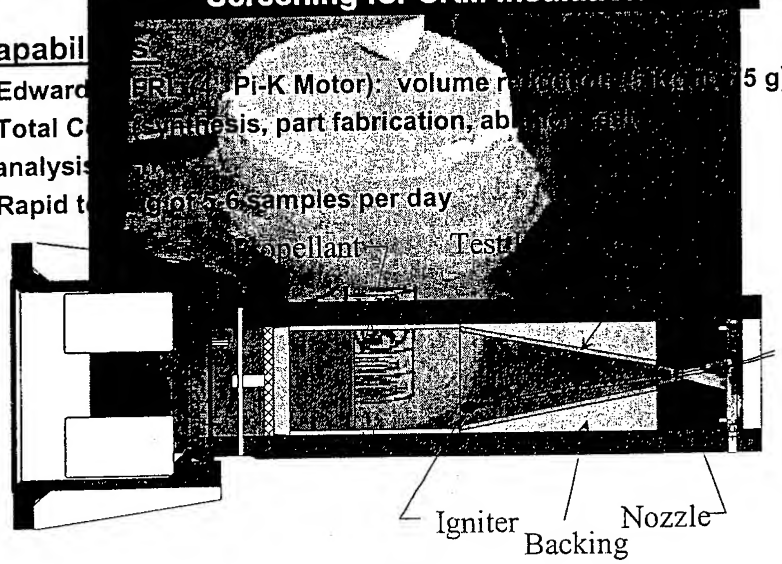
At 50 wt% loadings relative to a proprietary base-line material

Hardness:	15%↑	no change	17%↑
Tensile:	5%↓	27%↓	1%↓
Elongation:	no change	no change	no change
Viscosity:	35%↓	21%↓	36%↓
Density:	15%↑	3% ↓	12%↑

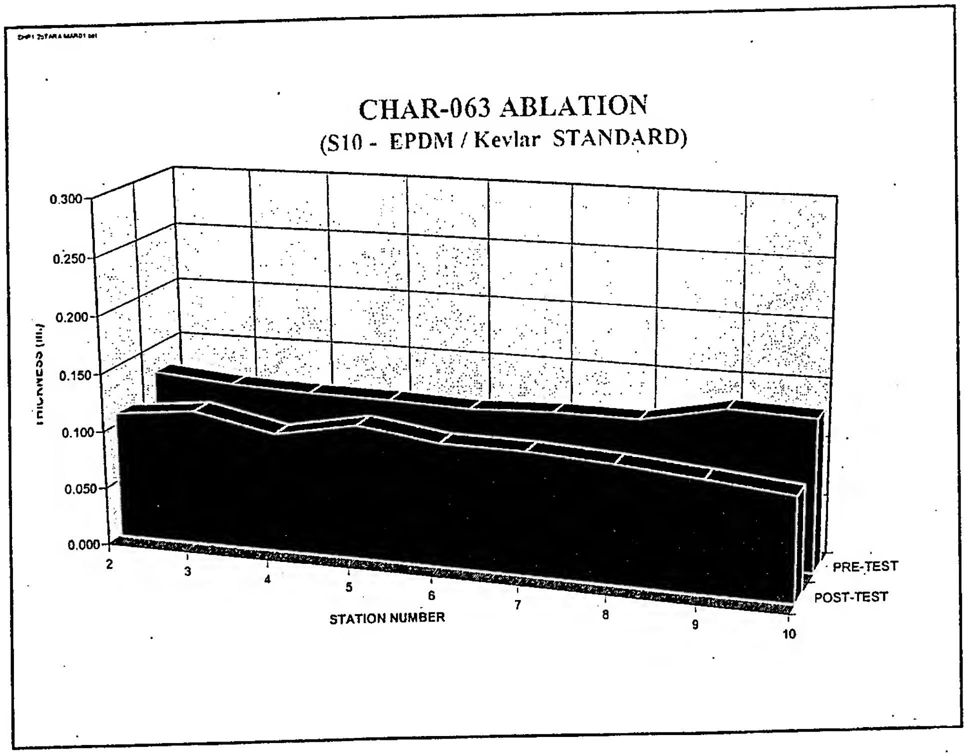
In-House SRM Insulation Testing

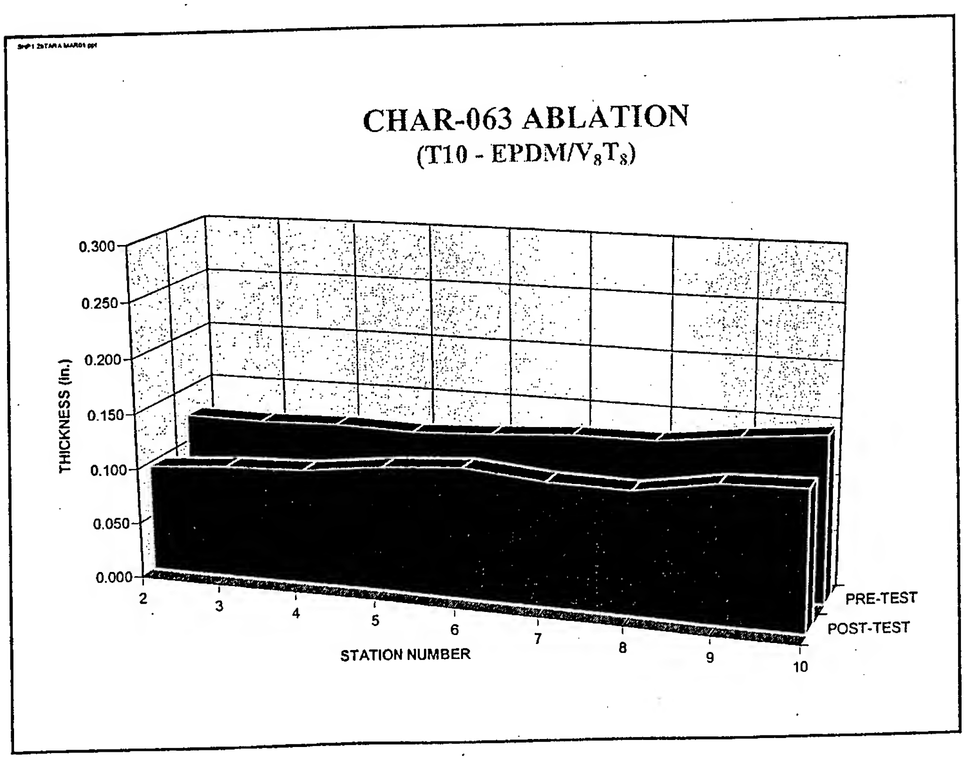
Objective: Low Cost/Low Volume Materials Screening for SRM Insulation

Capabil
- **Edward**
- **Total C analysi**
- **Rapid t**



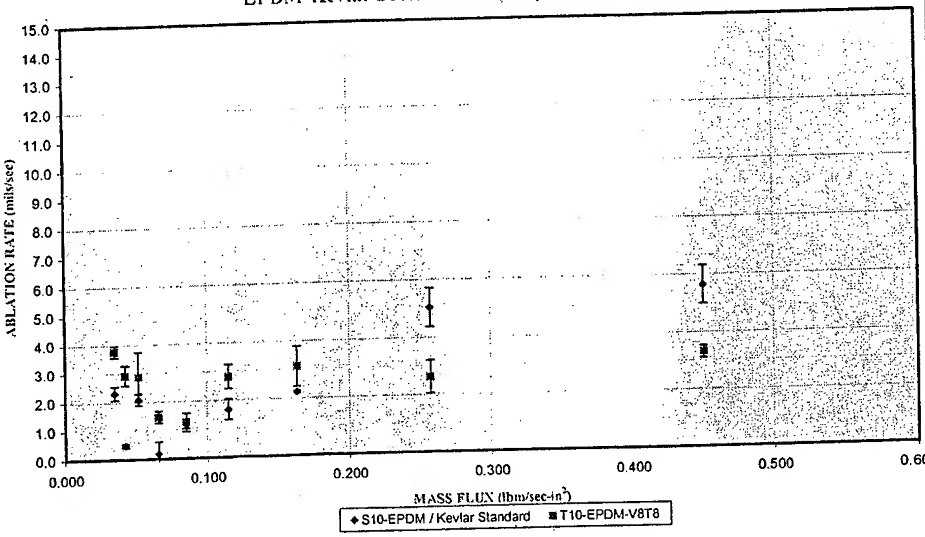
Firing Video clip


CHAR-063 ABLATION
(S10 - EPDM / Kevlar STANDARD)
THICKNESS (in.)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
2
3
4
5
6
7
8
9
10
STATION NUMBER
PRE-TEST
POST-TEST

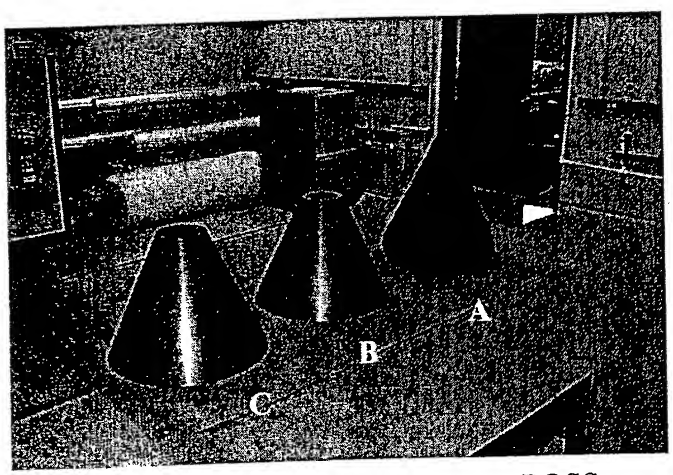

CHAR-063 ABLATION
(T10 - EPDM/V8T8)
THICKNESS (in.)
0.300
0.250
0.200
0.150
0.100
0.050
0.000
2
3
4
5
6
7
8
9
10
STATION NUMBER
PRE-TEST
POST-TEST

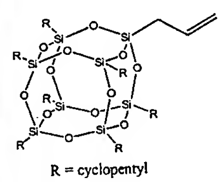
CHAR-063 ABLATION RATE

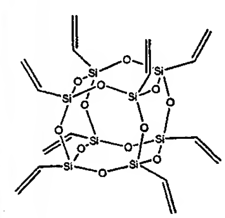
EPDM-Kevlar STANDARD (S10) / EPDM-V_8T_8 (T10)



Solid Rocket Motor~~s~~ Insulation

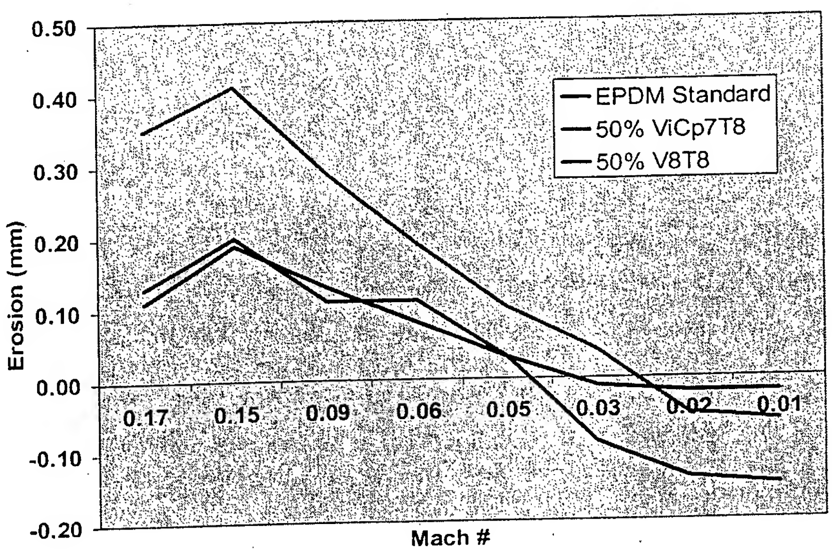






A) **Insulation containing POSS monomers**
B) **Convergent Cone**
C) **Convergent Cone + Insulation**

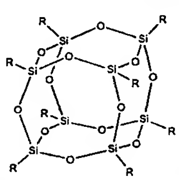
Convergent Cone SRM Insulation Tests



Negative numbers represent formation of structural char

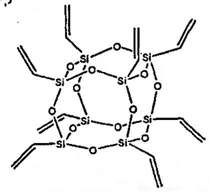
POSS Blends - Crystal Formation

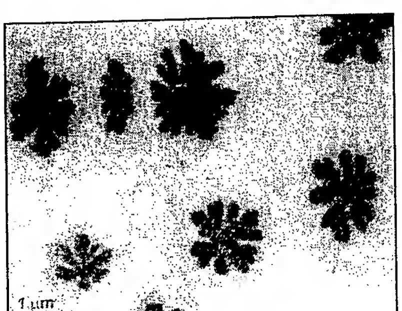
50 wt % POSS in 2 million mol. wt. Polystyrene



Cp_8T_8

Vi_8T_8

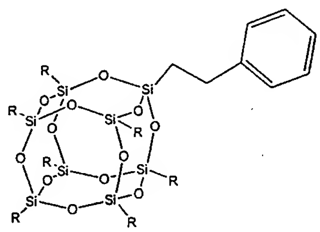




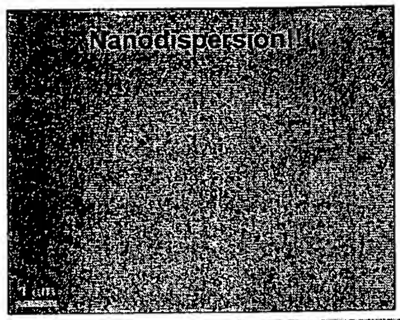
SEM image shows formation of immiscible POSS crystallites

POSS Blends - Miscibility

50 wt % Phenethyl$_8$T$_8$ in 2 million mol. wt. Polystyrene



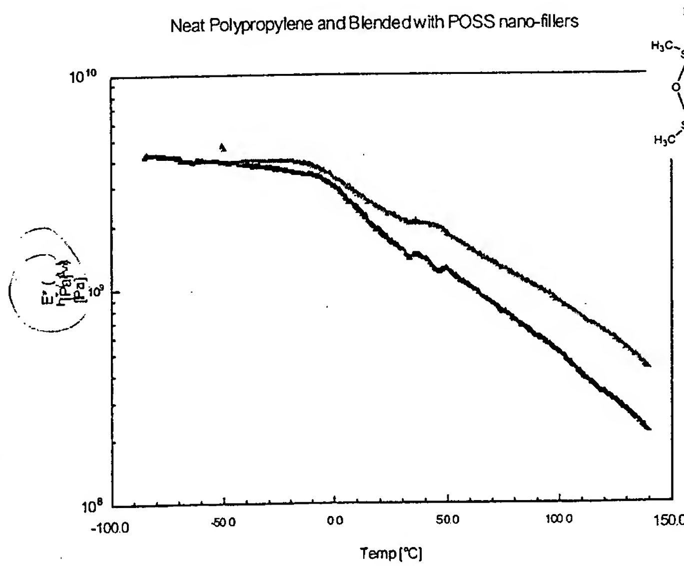
R = Phenethyl

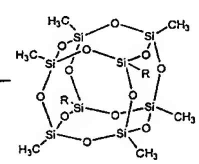


- Catalytic hydrogenation of Styryl$_8$T$_8$
- Demonstrated Complete Miscibility!!
- No POSS crystallites by SEM or X-ray!!

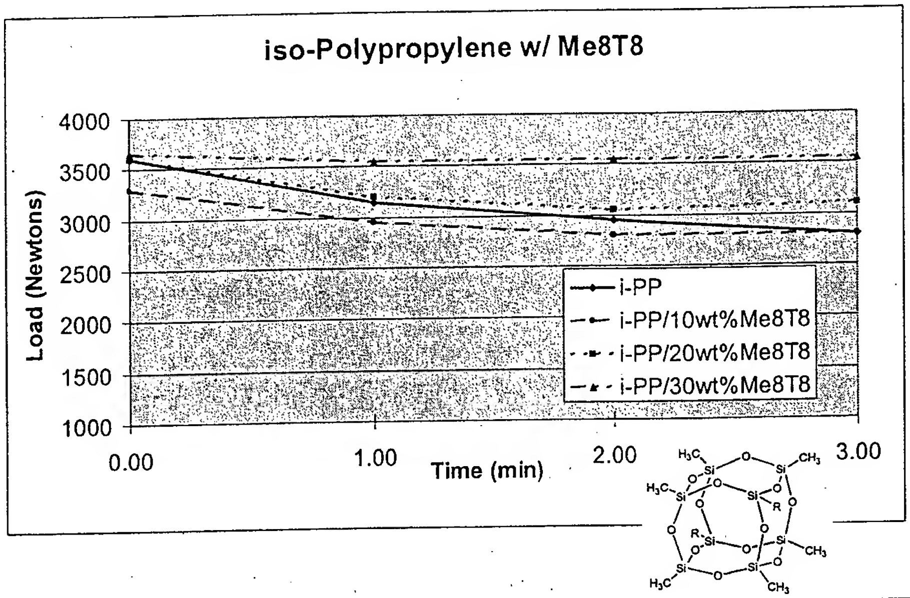
Scale-up, incorporation and testing polymer systems

i-PP/Me$_8$T$_8$ Processing Studies





i-PP/Me$_8$T$_8$ Processing Studies

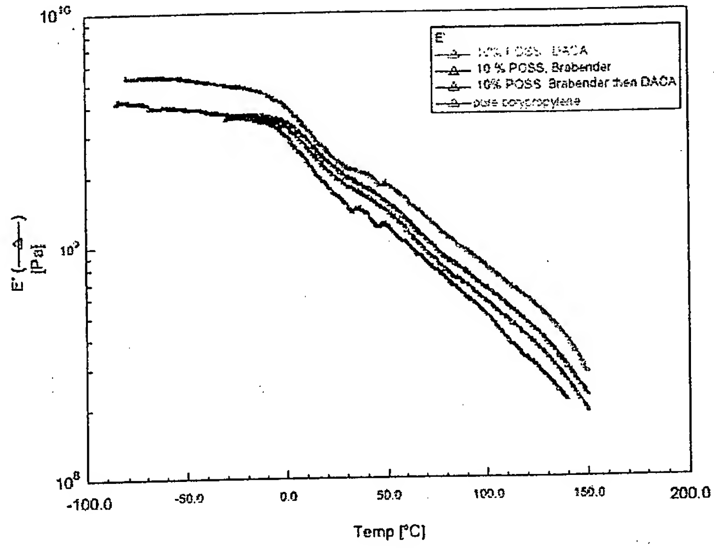


Prof. Andre Lee - Michigan State University

	Dow data	Neat *i*-PP (processed)	*i*-PP blended 2 wt% Methyl$_8$T$_8$	*i*-PP blended 5 wt% Methyl$_8$T$_8$	*i*-PP blended 10 wt% Methyl$_8$T$_8$
Tensile Strength @ Yield; ASTM D638	5000 psi (34.5 MPa)	4800 psi (33.0 MPa)	5000 psi (34.5 MPa)	5100 psi (35.1 MPa)	5200 psi (35.8 MPa)
Flexural Modulus (0.05 in/min, 1% secant); ASTM D790A	240,000 psi (1.655 GPa)	235,000 psi (1.620 GPa)	251,000 psi (1.730 GPa)	255,000 psi (1.757 GPa)	262,000 psi (1.80 GPa)
HDT @ 66 psi, as injected; ASTM D648	210 °F (99 °C)	210 °F (99 °C)	221 °F (105 °C)	239 °F (115 °C)	255 °F (124 °C)
Impact Izod @25C ASTM D256A	0.5 ft-lb/in	0.55 ft-lb/in	0.55 ft-lb/in	0.62 ft-lb/in	0.75 ft-lb/in

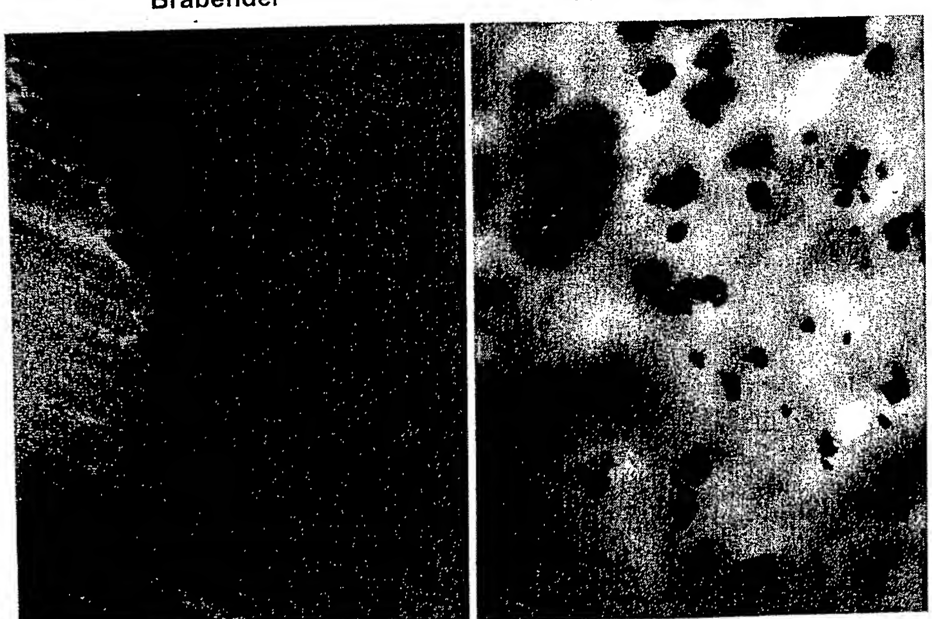
- The above data (other than Dow's data) is an average of at least 10 samples for each test with acceptable S.D. of 5% or better.

i-PP/Me$_8$T$_8$ Processing Studies

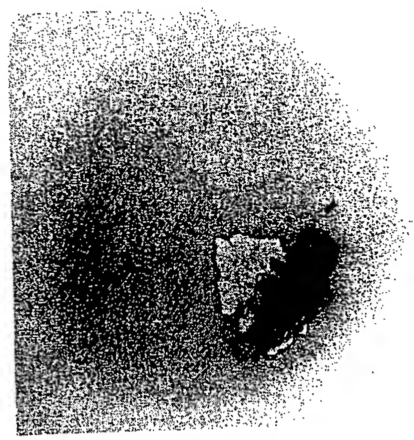


i-PP/Me8T8

Brabender | **Twin-Screw Extruder**



Shaw Industries i-PP/Me8T8 Fiber



Nanodispersion of Me8T8 around defect/dirt?

POSS-iPP Summary

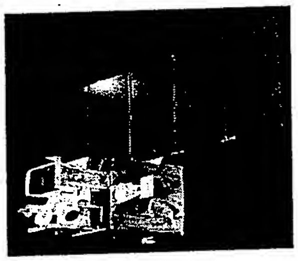
Prof. Ben Hsiao: SWAXS Studies

1) Some evidence of molecular dispersion of POSS in iPP - probably due to the favorable entropy of mixing between R (-CH_3) and the iPP chains

2) Half time of crystallization decreases by two orders of magnitude by flow (10^2 *vs.* 10^4 s). The addition of POSS further reduced the crystallization time - an indication of POSS being true molecular orientation enhancing agents (real nanocomposites)

3) In typical polymer processing, only the chains longer than M* can be oriented; chains shorter than M* remain unoriented due to fast relaxation. The addition of POSS appears to reduce the value of M* - more studies are needed!

Goal: Develop Multi-Functional, Space-Survivable Materials



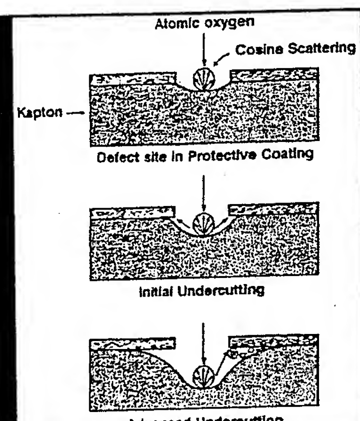
Satellites & Space Systems

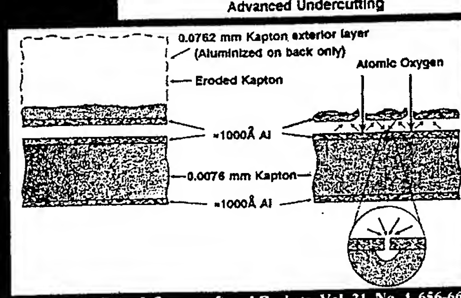
Bond	Dissociation Energy (EV)	λ (nm)	Material
$-C_6H_4-C(=O)-$	3.9	320	Kapton®
C-N	3.2	390	Kapton®
CF_3-CF_3	4.3	290	FEP Teflon®
CF_2-F	5.5	230	FEP Teflon®
Si-O	8.3	150	Nanocomposite
Zr-O	8.1	150	Nanocomposite
Al-O	5.3	230	Nanocomposite

Objectives

- Increase Space Resistance (AO, particle & VUV radiation, thermal cycling) of Polymeric Materials by 10x
- Self-Passivating/Self-Rigidizing/Self-Healing based on nanocomposite incorporation

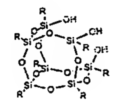
AO undercutting of LDEF Aluminized-Kapton Multilayer Insulation

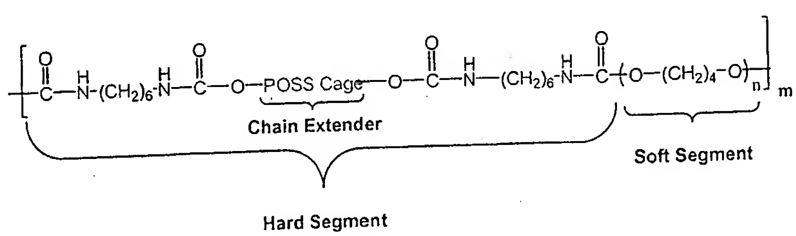




Groh, K.K., Banks, B.A., J. Spacecraft and Rockets, Vol. 31, No. 4, 656-664 (1994)

POSS-polyurethane Properties





POSS-polymer improvements

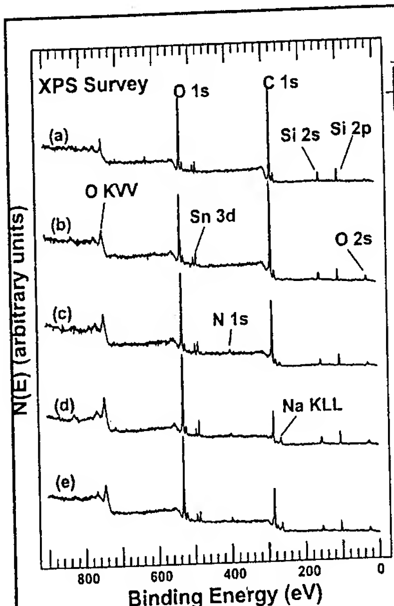
Up to 300 °C increase in the melt transition temperature (rheological studies show the transition from an oil to a true thermoplastic elastomer)

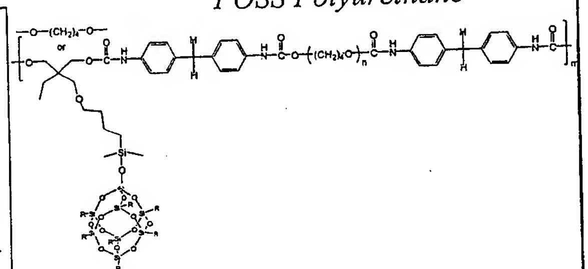
Up to a 100 °C increase in T_{dec} (29 wt% POSS, still TPE)

Up to 10X increase in moduli (>400% elongation with no destruction of hard segments))

17% POSS incorporation ----> 3X increase in Hardness (Shore A)

POSS Polyurethane





Sample Treatment	O	C	Si	Sn	Na	N
As entered	18.2	70.1	11.3	0.4	-	-
2.0-hr	17.5	70.2	11.2	0.7	0.4	-
24.0-hr	23.7	58.2	13.2	0.9	1.4	2.6
63.0-hr	35.3	37.3	20.4	1.3	3.0	2.7
3.3-h air	31.6	48.5	14.6	1.0	2.7	1.6

XPS Survey Spectra from a 60 wt% POSS-PU (a) after insertion into the vacuum system, (b) after a 2-hr (c) 24-hr and (d) 63-hr exposure to the hyperthermal AO flux, and (e) 3.3-hr air exposure following the 63-hr exposure.

Summary

- Successfully demonstrated multi-functionality of POSS utilizing both mechanical and physical properties
- We are looking into multiple applications for inorganic particles both as blends and copolymers
- Hybrid Plastics has been extremely successful in reducing the cost and increasing the production of POSS monomers
- Only with continued development of POSS monomers can we hope to control/predict property enhancements